

Observation of strong-coupling effects in a diluted magnetic semiconductor $\text{Ga}_{1-x}\text{Fe}_x\text{N}$

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A direct observation of the giant Zeeman splitting of the free excitons in $\text{Ga}_{1-x}\text{Fe}_x\text{N}$ is reported. The magneto-optical and magnetization data imply the ferromagnetic sign and a reduced magnitude of the effective p - d exchange energy governing the interaction between Fe^{3+} ions and holes in GaN, $N_0\beta^{(\text{app})} = +0.5 \pm 0.2$ eV. This finding corroborates the recent suggestion that the strong p - d hybridization specific to nitrides and oxides leads to significant renormalization of the valence band exchange splitting.

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A strong hybridization between anion p states and open d shells of transition metals (TM) is known to account for spin-dependent properties of magnetic isolators, semiconductors, and superconductors, such as antiferromagnetic superexchange, hole-mediated Zener ferromagnetism, and the contribution of spin fluctuations to Cooper pairing. Furthermore, the corresponding exchange splitting of the bands gives rise to giant magneto-optical and magnetotransport phenomena, a fingerprint of purposeful spintronic materials. Studies of the p - d exchange interaction have been particularly rewarding in the case of Mn-based II-VI dilute magnetic semiconductors (DMS) such as $(\text{Cd},\text{Mn})\text{Te}$ [1, 2]. In these systems, Mn is an isoelectronic impurity with a simple d^5 configuration, allowing a straightforward, quantitative determination of the p - d exchange integral β from the so-called giant Zeeman effect of the exciton: using the virtual crystal (VCA) and molecular-field approximations (MFA), one calculates a contribution to the spin splittings proportional to the Mn magnetization and to $N_0|\beta|$, where N_0 is the cation density. At the same time, the determination by photoemission spectroscopy [3], and the computation [4, 5], of band structure parameters demonstrated that the antiferromagnetic p - d exchange results indeed from p - d hybridization.

According to the above insight, in II-VI oxides and III-V nitrides, a small bond length and, thus, strong p - d hybridization, should result in particularly large values of $N_0|\beta|$, a prediction supported by photoemission experiments [6]. Surprisingly, however, some of the present authors found abnormally small exciton splittings in $(\text{Zn},\text{Co})\text{O}$ [7], $(\text{Zn},\text{Mn})\text{O}$ [8], and $(\text{Ga},\text{Mn})\text{N}$ [9]. Prompted by this contradiction, one of us suggested [10] that due to the strong p - d coupling, oxides and nitrides

form an outstanding class of DMS, in which VCA breaks down, making the *apparent* exchange splitting $N_0\beta^{(\text{app})}$ small and of opposite sign. Importantly, the system bears some similarity with semiconductor alloys such as $\text{Ga}(\text{As},\text{N})$, so that experimental and theoretical studies of the valence band exchange splitting in the strong coupling limit may significantly improve our understanding of these important alloys.

To check the above model, we have carried out high-resolution studies of magnetization and magnetoreflectivity in the free exciton region for $(\text{Ga},\text{Fe})\text{N}$ epitaxial layers, thoroughly characterized previously [11]. Since in GaN, in contrast to ZnO , the actual ordering of valence subbands is settled, the sign of $N_0\beta^{(\text{app})}$ can be unambiguously determined from polarization-resolved magneto-optical spectra. Furthermore, unlike Mn, Fe in GaN is an isoelectronic impurity with the simple d^5 configuration [11, 12], allowing a straightforward interpretation of the data. Our results lead to a value of $N_0\beta^{(\text{app})} = +0.5 \pm 0.2$ eV, which provides an important experimental support for the theory [10].

The $0.7 \mu\text{m}$ thick layers of $\text{Ga}_{1-x}\text{Fe}_x\text{N}$ were grown [11] by metalorganic vapor phase epitaxy (MOVPE), on [0001] sapphire substrates with a $1 \mu\text{m}$ thick, wide-band gap $(\text{Ga},\text{Al})\text{N}$ buffer layer, which is transparent in the free exciton region of $\text{Ga}_{1-x}\text{Fe}_x\text{N}$. The Fe flow rate was adjusted to keep the Fe content well below 0.4%, which is the solubility limit of Fe in GaN under our growth conditions. According to detailed luminescence, electron paramagnetic resonance, and magnetic susceptibility studies [11], in this range the Fe ions assume mostly the expected Fe^{3+} charge state corresponding to the d^5 configuration, for which the spin polarization as a function of temperature T and magnetic field B is determined

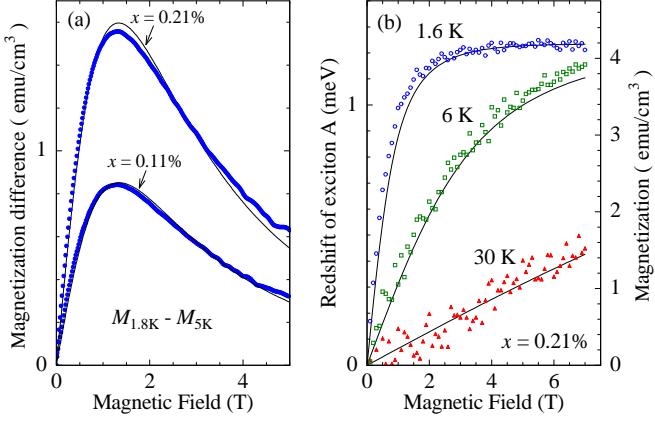


FIG. 1: (color online) (a) Difference between magnetizations measured (symbols) at 1.8 and 5 K. Same difference, computed (solid line) using the Brillouin function for $S = 5/2$ and treating the Fe concentration x as the only fitting parameter. (b) Comparison between the computed magnetization (solid lines, right axis) and the redshift of exciton A in σ^- polarization (symbols, left axis) for the 0.21% sample at three temperatures. The spectra are shown in Fig. 2(a).

by the Brillouin function $B_S(T, B)$ with spin $S = 5/2$ and Landé factor $g_{Fe^{3+}} = 2.0$. This is confirmed by our magneto-optical data shown in Fig. 1, which scale with $B_{5/2}(T, B)$. For the reported samples, we determine Fe content $0.11 \pm 0.02\%$ and $0.21 \pm 0.02\%$ by fitting the difference in magnetization values measured at 1.8 and 5.0 K up to 5 T in a high-field SQUID magnetometer, Fig. 1(a).

Magneto-reflectivity spectra were collected in the Faraday configuration (propagation of light and magnetic field along the normal to the sample, which is the c -axis of the wurtzite structure), and the light helicity σ^\pm defined with respect to the magnetic field direction. Owing to the high quality of the layers, either two, or the three, free excitons of GaN [13], A , B , C , are resolved, and their Zeeman shifts are visible in the spectra (Fig. 2). In σ^- polarization, the $A - B$ splitting increases and the $B - C$ splitting decreases with the field. Opposite shifts are observed in σ^+ . Since these shifts are entirely different from those observed in pure GaN [13], and related to the magnetization [Fig. 1(b)], we conclude that the Fe ions create a "giant Zeeman effect" in (Ga,Fe)N. Remarkably, however, the shift observed for A exciton is opposite in sign and significantly smaller at given x than in other wurtzite DMS with d^5 ions such as (Cd,Mn)Se [14].

We now describe the methodology that we employed to extract the values of the apparent $p-d$ exchange energy $N_0\beta^{(app)}$ for the valence band and the apparent $s-d$ exchange energy $N_0\alpha^{(app)}$ for the conduction band, from the reflectivity spectra. It involves two major steps. First, we calculate the reflection coefficients as a function of the photon energy, using a polariton model which incorporates the ground states of excitons A and B [7],

but also exciton C , excited states of excitons, and the continuum. Second, the field dependence of the exciton energies is calculated taking into account the essential features of the exciton physics in wide-band gap wurtzite DMS [7, 9].

The starting point of the polariton model is the dielectric function $\epsilon(\omega, k)$ containing polariton poles corresponding to excitons A and B [7, 15]: by solving analytically Eq. 3 of Ref. 15, we obtain the refractive index and then the reflection coefficient to be compared to experimental spectra. However, we replace the background dielectric function ϵ_0^* by the residual dielectric function $\epsilon^*(\omega)$, which takes into account additional contributions which are expected to exhibit no significant polariton effect [16]: exciton C , excited states of A , B and C [16] which are optically active (S -states), and transitions to the continuum of unbound states [17]. Hence

$$\epsilon^*(\omega) = \epsilon_0^* + 4\pi\alpha_{0C} \frac{\omega_C}{\omega_C^2 - \omega^2 - i\omega\Gamma_C} + \\ + \sum_{j=A,B,C} \left(\sum_{n=2}^{\infty} \frac{4\pi\alpha_{0j}}{n^3} \frac{\omega_{n,j}}{\omega_{n,j}^2 - \omega^2 - i\omega\Gamma_{n,j}} + \epsilon_{j,\text{ub}} \right). \quad (1)$$

Here $\epsilon_0^* = 5.2$ [16]; α_{0j} , $\omega_j = E_j/\hbar$, and Γ_j are the polarizability, resonant frequency, and damping rate of each exciton A , B , and C , treated as adjustable parameters (found to be close to those reported in Ref. 16). Resonant energies of the excited states n are $\hbar\omega_{n,j} = E_j + R_j^* - R_j^*/n^2$, where R_j^* are the effective Rydbergs known from our and other [18] studies of excitons in GaN. The corresponding damping parameters are calculated by using an empirical formula [18, 19], $\Gamma_{n,j} = \Gamma_\infty - (\Gamma_\infty - \Gamma_j)/n^2$, with one common damping rate Γ_∞ , which is an additional fitting parameter. Finally, the contribution $\epsilon_{j,\text{ub}}$ from unbound states is given in Eq. 5 of Ref. 17, with the amplitude determined by the exciton polarizabilities α_{0j} and the damping parameter $\Gamma_\infty/2$ [16, 20]. Calculated reflectivity spectra are compared to experimental ones in Figs. 2(a,c), and the exciton energies are displayed as a function of the magnetic field in Fig. 2(b,d).

In the second step, the field dependence of the exciton energies is calculated for the hamiltonian

$$H = E_0 + H_v + H_{e-h} + H_Z + H_{\text{diam}} + H_{sp-d}^{(\text{app})}, \quad (2)$$

where E_0 is the band-gap energy and H_v describes the top of the valence band in semiconductors with the wurtzite structure [21, 22, 23]. This term includes the trigonal component of both crystal field and biaxial strain (described by the parameter $\tilde{\Delta}_1$) as well as the anisotropic spin-orbit interaction (characterized by Δ_2 and $\Delta_3 = 5.5$ meV [22] for the direction parallel and perpendicular to the c -axis, respectively). The component H_{e-h} describes the electron-hole interaction within the exciton [7, 9, 13, 23] and it involves the effective Rydberg and the electron-hole exchange integral $\gamma = 0.6$ meV [23].

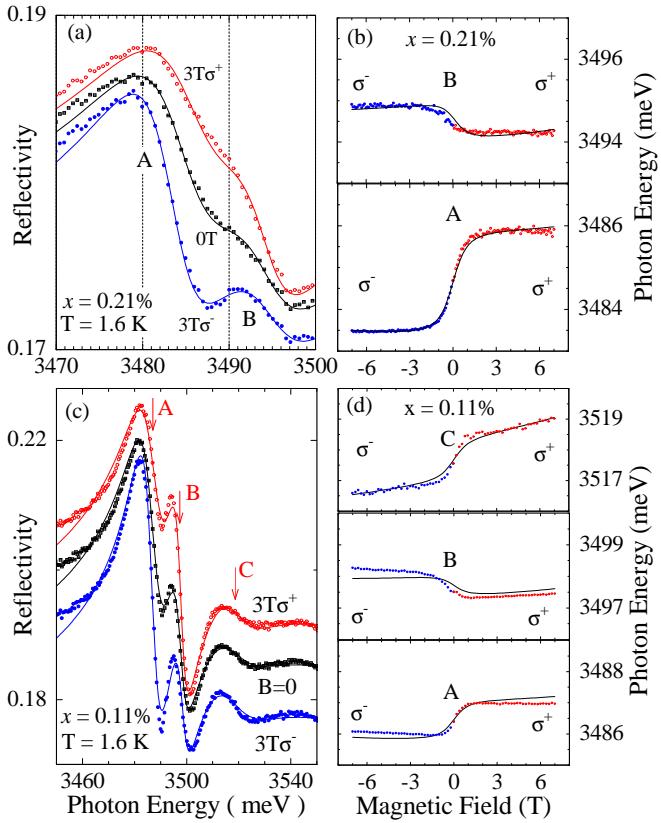


FIG. 2: (color online) Reflectivity of $\text{Ga}_{1-x}\text{Fe}_x\text{N}$ in Faraday configuration at 1.6 K for $x = 0.21\%$ (a) and 0.11% (c) where particularly well resolved excitons A , B , and C are visible in σ^- polarization. (b,d) Field-induced exciton shifts of the excitons determined from the polariton model (points) compared to the expectations of the exciton model (solid lines). The determined values of the exciton and exchange parameters are shown in Table I.

Effects linear in the magnetic field are taken into account by the standard Zeeman hamiltonian H_Z [13, 21], parameterized by the effective Landé factor $g_e = 1.95$ for the electrons and the relevant Luttinger effective parameter $\tilde{\kappa} = -0.36$ that describes the splitting of all three valence subbands [13]. The diamagnetic shift is described by a single term quadratic in the magnetic field, $H_{\text{diam}} = dB^2$, where $d = 1.8 \mu\text{eV}/\text{T}^2$ [13]. Finally, $H_{sp-d}^{(\text{app})}$ is the exchange interaction between Fe ions and carriers in the extended states from which the excitons are formed. We use the standard form of the $s,p-d$ hamiltonian [1, 2, 14], which is proportional to the scalar product of the carrier spin and the magnetization. However, being aware that these splittings can have a different meaning from the usual one [10, 24], we use effective quantities $\alpha^{(\text{app})}$ and $\beta^{(\text{app})}$. The field dependence of the exciton energies, calculated with the values of fitting parameters collected in Table I, is compared with the experimental results in Fig. 2(b,d).

The detailed analysis of this hamiltonian [9] shows that

x	$N_0(\beta^{(\text{app})}-\alpha^{(\text{app})})$	$N_0(\beta^{(\text{app})}+\alpha^{(\text{app})})$	E_A	$\tilde{\Delta}_1$	Δ_2
0.11%	0.44 ± 0.2	0.60 ± 0.2	3.4864	19.4	7.5
0.21%	0.46 ± 0.1	0.63 ± 0.3	3.4846	15.5	7.2

TABLE I: Fitting parameters describing the exciton energies and the giant Zeeman effect shown in Fig. 2(b,d). Units are eV, except for $\tilde{\Delta}_1$ and Δ_2 , which are given in meV.

the giant Zeeman shifts of excitons A and B are mainly governed by $N_0\beta^{(\text{app})}-N_0\alpha^{(\text{app})}$. Moreover, exciton A , which in GaN is formed from valence band states with parallel spin and orbit (Γ_9 state), shifts to low energies in σ^- polarization: hence the exchange integral difference $N_0\beta^{(\text{app})}-N_0\alpha^{(\text{app})}$ is positive. At the same time, exciton B is mixed with exciton C , whose shift is primarily controlled by $N_0\beta^{(\text{app})}+N_0\alpha^{(\text{app})}$. Hence, by incorporating exciton C in our description of the reflectivity spectra, we can evaluate independently the apparent exchange energy $N_0\beta^{(\text{app})}$ for the valence band and the apparent exchange energy $N_0\alpha^{(\text{app})}$ for the conduction band. This determination is quite accurate in the case of the 0.11% sample, for which exciton C is spectrally well resolved, but an estimation is still possible in the 0.21% sample through its effect on exciton B . From the shifts of B and C , we find that the sign of $N_0\beta^{(\text{app})}+N_0\alpha^{(\text{app})}$ is also positive, and its value is quite close to that of $N_0\beta^{(\text{app})}-N_0\alpha^{(\text{app})}$, see Table I. Hence, $|N_0\alpha^{(\text{app})}|$ is much smaller than $|N_0\beta^{(\text{app})}|$, and $N_0\beta^{(\text{app})}$ is positive. More precisely, the complete fit yields the values of the exchange energies $N_0\beta^{(\text{app})} = +0.5 \pm 0.2$ eV and $N_0\alpha^{(\text{app})} = +0.1 \pm 0.2$ eV.

We note that our evaluation of $N_0\alpha^{(\text{app})}$ includes within the experimental error the values of $N_0\alpha = 0.25 \pm 0.06$ eV found in early studies of Mn-based II-VI DMS [2]. We have no reason to question here the applicability of the standard description of the conduction band in $(\text{Ga},\text{Fe})\text{N}$ – contrary to $(\text{Ga},\text{Mn})\text{As}$ and $(\text{Ga},\text{Mn})\text{N}$, for which the magnitudes of $N_0\alpha^{(\text{app})}$ were found to be reduced under some experimental conditions [24].

For the expected d level arrangement, both the ferromagnetic sign and the small magnitude of the apparent $p-d$ exchange energy are surprising. Indeed, in GaN, the Fe d^5/d^6 acceptor-like level resides less than 3 eV above the top of the valence band [12]. This state, $e_g\downarrow$, and also the higher lying $t_2\downarrow$ level that can hybridize with the valence band states, remain unoccupied in intrinsic $(\text{Ga},\text{Fe})\text{N}$. At the same time, no donor-like d^5/d^4 state has been found within the GaN gap. This could be expected, as in the TM series a particularly large correlation energy U separates the d^5 and d^6 shells. Hence, the occupied Fe $t_2\uparrow$ levels reside within the valence band. According to the Schrieffer-Wolf theory, in such a case the $p-d$ exchange coupling is antiferromagnetic: this was confirmed by magnetooptical studies of tellurides and selenides containing either Mn or Fe, including stud-

ies carried out in our labs, which lead systematically to $N_0\beta = -1.4 \pm 0.5$ eV [2].

However, it has been recently remarked [10] that for an appropriately strong TM potential, like the one expected for oxides and nitrides, the TM ion can bind a hole – a trend which was already suggested by strong deviations from the VCA in (Cd,Mn)S [25] and by the analysis of *ab initio* calculations [26]. A summation of infinite series of relevant self-energy diagrams demonstrates that in such a situation, the spin splitting of extended states involved in the optical transitions remains proportional to magnetization of the localized spins, but the apparent exchange energy becomes significantly renormalized [10]. In fact, for the expected coupling strength, the theory predicts $-1 < \beta^{(\text{app})}/\beta < 0$, as observed here for (Ga,Fe)N.

A fruitful comparison can be made with the modification of the conduction band of GaAs induced by a slight doping with Nitrogen [27]. When a hydrostatic pressure is applied, the Nitrogen isoelectronic centers create localized states, which are observed in photoluminescence, but also extended states (the so-called E^+ states) to which the oscillator strength is transferred so that they are observed in reflectivity; moreover, these optically active states exhibit an anticrossing with the localized states, and the strength of the anticrossing increases with the Nitrogen density. As a result, the transition to these E^+ states exhibits a shift to *high energy* when the density of *low energy states* increases. In a DMS with a large value of $N_0|\beta|$, only the TM impurities with the right spin orientation (antiparallel to the hole spin) are expected to form a localizing center [10, 25]: hence the giant Zeeman shift in (Ga,Fe)N can be understood as resulting from a similar anticrossing but in this case the density of relevant localized centers is additionally controlled by the field-induced orientation of the localized spins.

In conclusion, giant Zeeman splitting has been observed by magnetoreflectivity for the *A*, *B*, and *C* excitons in $\text{Ga}_{1-x}\text{Fe}_x\text{N}$. The spectra are well described by the exciton model valid for DMS with the wurtzite structure. The determined sign and magnitude of the *apparent p-d* exchange energy $N_0\beta^{(\text{app})} = +0.5 \pm 0.2$ eV constitutes an important verification of a recent theory [10], which describes the effects of the *p-d* interaction circumventing the virtual-crystal and molecular-field approximations that break down in nitrides and oxides. In these systems, TM ions bind holes, precluding in this way the occurrence of carrier-mediated ferromagnetism in *p*-type materials. However, at sufficiently high hole densities, an insulator-to-metal transition is expected. In the metallic phase, many-body screening of local potentials annihilates bound states. Large spin-splitting and robust ferromagnetism are expected in this regime [28, 29].

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- [1] J. K. Furdyna and J. Kossut, eds., *Diluted Magnetic Semiconductors*, vol. 25 of *Semiconductors and Semimetals* (Academic Press, New York, 1988).
- [2] P. Kacman, *Semicond. Sci. Technol.* **16**, R25 (2001), and references cited therein.
- [3] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, and M. Kawasaki, *Phys. Rev. B* **65**, 085209 (2002).
- [4] A. Zunger, *Solid State Phys.* vol. **39**, 275 (1986).
- [5] B. E. Larson, K. C. Hass, E. Ehrenreich, and A. E. Carlsson, *Phys. Rev. B* **37**, 4137 (1988).
- [6] J. I. Hwang, Y. Ishida, M. Kobayashi, H. Hirata, K. Takubo, T. Mizokawa, A. Fujimori, J. Okamoto, K. Mamiya, Y. Saito, *et al.*, *Phys. Rev. B* **72**, 085216 (2005).
- [7] W. Pacuski, D. Ferrand, J. Cibert, C. Deparis, J. A. Gaj, P. Kossacki, C. Morhain, *Phys. Rev. B* **73**, 035214 (2006).
- [8] E. Przeździecka, E. Kamińska, M. Kiecan, M. Sawicki, L. Kłopotowski, W. Pacuski, and J. Kossut, *Solid State Commun.* **139**, 541 (2006).
- [9] W. Pacuski, D. Ferrand, J. Cibert, J. A. Gaj, A. Gohlik, P. Kossacki, S. Marcet, E. Sarigiannidou, and H. Mariette, *cond-mat/0703041*.
- [10] T. Dietl, *cond-mat/0703278*.
- [11] A. Bonanni, M. Kiecan, C. Simbrunner, T. Li, M. Sawicki, M. Wegscheider, M. Quast, H. Przybylińska, A. Navarro-Quezada, R. Jakiel, *et al.*, *Phys. Rev. B* **75**, 125210 (2007).
- [12] E. Malguth, A. Hoffmann, W. Gehlhoff, O. Gelhausen, M. R. Phillips, and X. Xu, *Phys. Rev. B* **74**, 165202 (2006), and references cited therein.
- [13] R. Stępniewski, M. Potemski, A. Wysmołek, K. Pakula, J. M. Baranowski, J. Lusakowski, I. Grzegory, S. Porowski, G. Martinez, and P. Wyder, *Phys. Rev. B* **60**, 4438 (1999).
- [14] M. Arciszewska and M. Nawrocki, *J. Phys. Chem. Solids* **47**, 309 (1986).
- [15] J. Lagois, *Phys. Rev. B* **16**, 1699 (1977).
- [16] R. Stępniewski, K. P. Korona, A. Wysmołek, J. M. Baranowski, K. Pakuła, M. Potemski, G. Martinez, I. Grzegory, and S. Porowski, *Phys. Rev. B* **56**, 15151 (1997).
- [17] C. Tanguy, *Phys. Rev. Lett.* **75**, 4090 (1995).
- [18] K. Kornitzer, T. Ebner, M. Grehl, K. Thonke, R. Sauer, C. Kirchner, V. Schwegler, M. Kamp, M. Leszczynski, I. Grzegory, *et al.*, *Phys. Stat. Sol. B* **216**, 5 (1999).
- [19] R. Le Toullec, N. Piccioli, and J. C. Chervin, *Phys. Rev. B* **22**, 6162 (1980).
- [20] B. Sermage, S. Petiot, C. Tanguy, Le Si Dang, and R. André, *J. Appl. Phys.* **83**, 7903 (1998).
- [21] G. L. Bir and G. E. Pikus, in *Symmetry and Strain-Induced Effects in Semiconductors* (Halsted, Jerusalem, 1974).
- [22] B. Gil, O. Briot, and R. L. Aulombard, *Phys. Rev. B* **52**, R17028 (1995).
- [23] M. Julier, J. Campo, B. Gil, J. P. Lascaray, S. Nakamura, *Phys. Rev. B* **57**, R6791 (1998).
- [24] C. Śliwa and T. Dietl, *cond-mat/0707.3542*.
- [25] C. Benoît à la Guillaume, D. Scalbert, and T. Dietl, *Phys.*

Rev. B **46**, 9853 (1992).

[26] R. Bouzerar, G. Bouzerar, and T. Ziman, *Europhys. Lett.* **78**, 67003 (2007).

[27] J. Wu, W. Shan, and W. Walukiewicz, *Semicond. Sci. Technol.* **17**, 860 (2002), and references cited therein.

[28] T. Dietl, F. Matsukura, and H. Ohno, *Phys. Rev. B* **66**, 033203 (2002).

[29] F. Popescu, C. Sen, E. Dagotto, and A. Moreo, cond-mat/0705.0309, and references cited therein.